The Reaction of Gaseous Acetic Anhydride With Coal

Paul Fugassi, Ruth Trammell[1] and Philip Masciantonio

Coal Research Laboratory, Department of Chemistry
Carnegie Institute of Technology, Pittsburgh (13) Penna.

A number of coals of the bituminous and sub-bituminous ranks have been acetylated at 45°C. using acetic anhydride vapor at a relative pressure of unity. Acetylation by this procedure gives hydroxyl contents less than that determined by the trimethylsilyl ether method for bituminous coals but higher hydroxyl contents for sub-bituminous coals. It is suggested that acetic anhydride reacts with carboxyl groups to give mixed acid anhydrides and the higher values obtained for sub-bituminous coals is due to the carboxyl group content of such coals. Oxygen gas catalyzes the acetylation of sub-bituminous coals and until the effect of oxygen is investigated in detail, acetylation of lower rank coals with acetic anhydride should be done in the absence of oxygen.

[1]Present address, Dept. of Chemistry, Chatham College, Pittsburgh (13) Pa.

Not for Publication
Presented Before the Division of Gas and Fuel Chemistry
American Chemical Society
Chicago, Illinois, Meeting, September 7-12, 1958

The Reaction of Gaseous Acetic Anhydride With Coal

Paul Fugassi, Ruth Trammell[1] and Philip Masciantonio
Coal Research Laboratory, Dept. of Chemistry
Carnegie Institute of Technology, Pittsburgh (13), Pa.

1. Present address, Dept. of Chemistry, Chatham College, Pittsburgh (13), Pa.

Introduction

The hydroxyl contents of coals have been measured by a number of different methods and the results of such work have been summarized by Blom, Edelhausen and Van Krevelen(1). In general methods using different reagents give different hydroxyl contents for coals of the same rank. Even in cases where the same reagent has been employed by different investigators there is not close agreement on the hydroxyl content.

It is the object of this communication to report some experimental work on bituminous and sub-bituminous coals wherein the coals are reacted at 45°C. with gaseous acetic anhydride at a relative pressure close to unity. In comparison to other acetylation work on coal using acetic anhydride, the temperatures employed here are much lower and the reaction times much longer. The extent of the reaction is followed gravimetrically.

Experimental

Apparatus: Measurements were made using McBain-Bakr balances housed in an air thermostat held at 45°C. ± 0.1°. Because of the corrosive nature of acetic anhydride--acetic acid mixtures, springs made from fine tungsten wire were used. These springs had sensitivities ranging from 3.81 to 4.86 milligrams per millimeter extension. Spring displacements were measured to 0.1 mm using a cathetometer. With sample weights of the order of 500 milligrams the precision is about one part in a thousand.

Chemicals: Acetic anhydride, benzene, and pyridine were freshly distilled before use and stored over Drierite. The following coals of bituminous rank were used: Upper Kittanning, Upper Freeport, Pittsburgh, Bruceton and Bruceton anthraxylon. The coals of sub-bituminous rank were Wyoming (Elkol), Wyoming (Rock Springs), Illinois No. 6 (Clinton), and Illinois No. 6 (Jefferson). The analyses for Wyoming (Rock Springs), Bruceton, Bruceton anthraxylon, and Illinois No. 6 (Jefferson) have been previously published(2). The analyses for the other coals are given in Table I.

Table I
Ultimate Analyses (Moisture Free Basis)

Coal	C	H	N	O	S	Ash
Upper Kittanning	80.6	3.8	1.1	3.7	1.3	9.5
Upper Freeport	78.7	4.8	0.9	4.6	1.7	9.3
Pittsburgh	76.0	5.1	1.5	7.6	1.6	8.2
Wyoming (Elkol)	74.3	5.3	1.2	15.2	0.6	3.4
Illinois No. 6 (Jefferson)	65.2	4.9	1.2	10.4	4.0	14.3

The samples of Upper Kittanning, Upper Freeport, and Pittsburgh coals are standard samples of the Coal Research Board, Commonwealth of Pennsylvania, and were used as received. Samples of Wyoming (Rock Springs), Illinois No. 6 (Jefferson) and Bruceton coals were furnished by the Bruceton Station, U. S. Bureau of Mines and were used as received. Wyoming (Elkol) and Illinois No. 6 (Clinton) were available in bulk. These samples were ground by passage through a hammer mill and used unsieved.

Procedure: The samples of coal, placed in small glass buckets were weighed to 0.1 mg. and allowed to stand overnight in a desiccator. The samples, after being reweighed, were attached to the springs and allowed to stand for one hour, with an atmosphere of air present, to come to thermostat temperature. The extension of the spring was then measured. It is assumed that the weight of the sample had not changed during the hour waiting period. The apparatus was then evacuated and the extension of the springs measured. Usually samples came to constant weight in 8 hours, however evacuation was continued for a minimum of 24 hours.

After the system was closed off from the pumping system, acetic anhydride was admitted at a relative pressure of unity (about 12 mm.) and the system allowed to stand. Readings of the spring extension were taken until the weights of the sample were practically constant. At this point, the system was evacuated for several days and the weight of the sample measured. Gaseous acetic anhydride was then re-admitted and the samples allowed to stand until their weights reached a constant value. Evacuation of the system for several days followed by measurement of the weights of the samples then gave the increase in weight of the sample due to acetylation. In most cases samples of coal were subjected to two consecutive anhydride treatments before the final reading was taken. In a few cases three consecutive anhydride treatments were employed but little or no increase in weight resulted from the third treatment with acetic anhydride.

Discussion

Catalysis: The vapor phase acetylation of coals at 45°C. is a very slow process so a number of qualitative experiments were made with Illinois No. 6 (Clinton) coal to determine if the rate could be accelerated.

Coal is a gel and it is known that for other gels, such as cellulose, acetic anhydride is a poor swelling agent and that for cellulose the rate of acetylation can be increased by the use of suitable swelling agents. The behavior of acetic anhydride with respect to cellulose suggests the use of swelling agents in coal acetylation.

Methanol swells coal so several experiments were made in which the coal before acetylation was exposed to methanol vapor at 45°C. and the methanol

vapor desorbed before acetylation. Methanol is reversibly desorbed and no increase in acetylation rate was noted.

Pyridine swells coal but pyridine is sorbed irreversibly by coal. Coal treated with pyridine vapor, evacuated, and then acetylated showed an increased rate of acetylation. Unfortunately the irreversible sorption of pyridine is large and although the amount of this irreversible sorption on coal can be measured accurately, it is not possible to assume that the amount of pyridine sorbed irreversibly by the coal does not change as the coal is acetylated. For this reason the overall weight change might not be a measure of the extent of acetylation.

Benzene vapor at 45°C. is irreversibly sorbed by coal in amounts ranging from 0.0 to 23.4 milligrams per gram of coal. A coal sample exposed to benzene vapor, evacuated, and then acetylated appears to acetylate faster. However, the increase in rate of acetylation is not striking.

Consequently the experiments made here used acetic anhydride alone. As a consequence of the acetylation reaction acetic acid is present and serves to some extent as a swelling agent. On Illinois No. 6 (Clinton) coal it has been shown that acetic acid vapor is reversibly desorbed on coal previously acetylated with acetic anhydride.

Effect of Oxygen: In carrying out the acetylations it was noted that while the coals of bituminous rank gave reproducible increases in weight within ± 5%, the coals of sub-bituminous rank would sometimes give high values and in other experiments low values. Although all samples were evacuated for at least 24 hours using a two stage mercury vapor pump, the system could not be baked out and small but variable amounts of oxygen might be present in individual sets of experiments. Whenever a small amount of oxygen, 5 mm., was added to the system the results became more reproducible and it appears, for sub-bituminous coals, oxygen has a catalytic effect. However the presence of oxygen introduces the possibility of an oxidation of the coal. To check this point five coal samples after the usual evacuation were exposed to 5 mm. of oxygen, with no anhydride present, for a period of 21 days. The experimental results are tabulated in Table II and are the increases in weight after evacuation.

Table II
Oxidation of Coals; 5 mm. O_2, 21 days at 45°C.

Coal	Upper Kittanning	Upper Freeport	Pittsburgh	Illinois (Clinton)	Wyoming (Elkol)
Wt. Increase mg/gram	4.1	1.8	2.0	11.2	13.5

It will be noted that the first three coals of bituminous rank show little or no change in weight. The two sub-bituminous coals, Illinois (Clinton) and Wyoming (Elkol) show relatively greater changes in weight. Pressure changes during these experiments were negligible and it was concluded that oxidation under the experimental conditions used was a very slow process relative to the slow acetylation reaction.

Acetylation: Most of the acetylation experiments were made with 5 mm of oxygen present but sufficient data with no added oxygen are available to indicate that the presence of oxygen has little or no effect on the weight increase for

bituminous coals. The acetylation data are tabulated in Table III. These data are all for experiments at 45°C., with a relative pressure of acetic anhydride of unity and include, in the average weight increase, experiments with and without added oxygen. All samples were given at least two consecutive treatments with acetic anhydride and in some cases three consecutive treatments. The spread of the individual values from the average is within ± 5%. Reaction times ranged from 23 to 37 days.

Table III
Acetylation Data (45°C.)

Coal	Average Wt. Increase ($\frac{\text{milligrams}}{\text{gram}}$)
Upper Kittanning	32
Upper Freeport	30
Pittsburgh	24
Bruceton Anthraxylon	13
Bruceton	78
Illinois No. 6 (Clinton)	140
Illinois No. 6 (Jefferson)	158
Wyoming (Rock Springs)	143
Wyoming (Elkol)	175

Calculation of Hydroxyl Content: If it is assumed that the increase in weight of the coal sample is caused mainly by replacement of a hydrogen atom from an hydroxyl group by the acetyl radical then the weight increase divided by 42 will give millimoles of hydroxyl groups per gram of coal (m.f. basis). The implications of such an assumption will be discussed. Processes leading to a weight increase other than replacement of hydrogen by the acetyl group might be 1. Irreversible sorption of acetic anhydride, 2. Irreversible sorption of acetic acid resulting from the acetylation process and 3. Reaction of acetic acid with salts of weak acids, such as pyrites, present in the coal. There is no independent evidence which indicates the magnitude of irreversibility of acetic anhydride sorption on coal. However the hydroxyl content as calculated assuming no trapped acetic anhydride is already low relative to the values obtained by other methods for coals of the bituminous rank. The effect of trapped acetic anhydride would be to make these values lower still. With regard to acetic acid it has been shown that acetic acid sorption is reversible on acetylated Illinois coal. This fact suggests that the amount of acetic acid trapped must be small. The reaction of acetic acid with pyrites can be assumed to give sulfur, iron acetate, and hydrogen sulfide. Assuming a 500 milligram sample containing 1% of iron sulfide, the weight increase would be around 2.9 milligrams per gram of coal if hydrogen sulfide is lost on evacuation. From other experiments it is known that the evaporation of elemental sulfur at 45°C. is very slow.

For four of the coals used data on the hydroxyl content are available as determined by the trimethylsilyl ether method(2). A comparison of these data with the data obtained by acetylation is given in Table IV.

Table IV
Hydroxyl Content of Coals (millimoles per gram)

Coal	Acetylation (Vapor)	Trimethylsilyl Ether
Bruceton Anthraxylon	0.3	2.3
Bruceton	1.9	2.3
Wyoming (Rock Springs)	3.4	2.8
Illinois No. 6 (Jefferson)	3.8	3.4

For the bituminous coal the hydroxyl content as determined by acetylation is lower than that obtained by the trimethylsilyl ether method. One presumes that certain sterically hindered hydroxyl groups react very slowly with acetic anhydride. On the other hand the hydroxyl content as determined by acetylation is higher for two sub-bituminous coals. Although it is known(3) that certain polycyclic structures photo-oxidize readily in the presence of acetic anhydride and oxygen such a reaction is excluded here because 1. Acetylation experiments with light excluded gave about the same weight increases as with light present and 2. No decrease in pressure caused by oxygen consumption was observed. However it is known that sub-bituminous coals contain carboxylic acid groups and the possibility exists that with sub-bituminous coals acetic anhydride reacts with acidic groups to form mixed anhydrides in addition to reacting with hydroxyl groups to form esters. The mixed anhydride would be expected to react with water more rapidly at a given temperature than the ester. Accordingly a series of five coals were acetylated and then exposed to water vapor at 20 mm pressure at 45°C. The results of these hydrolysis experiments are shown in Table V.

Table V
Hydrolysis of Acetylated Coals (45°C.)

Coal	Exposure Time H_2O (20 mm.)	Relative Weight
Upper Kittanning	0 hours	1.00
	1	1.00
	3	1.06
	22	1.00
	70	0.90
Upper Freeport	0	1.00
	1	1.10
	3	1.15
	22	1.15
	70	0.89
Pittsburgh	0	1.00
	1	1.08
	3	1.08
	22	1.08
	70	1.00
Illinois No. 6 (Clinton)	0	1.00
	1	0.95
	3	0.95
	22	0.91
	70	0.86
Wyoming (Elkol)	0	1.00
	1	0.94
	3	0.92
	22	0.90
	70	0.81

Comparison of these data indicate that the three bituminous coals show small changes in weight on treatment with water even for periods as long as 70 hours. This indicates that the ester group present is relatively stable to the action of water vapor. On the other hand the two sub-bituminous coals show greater decreases in weight under the same conditions. It appears probable that acetylated sub-bituminous coals contain groups which differ in their behavior with respect to water stability and as has been mentioned the mixed anhydride group from its known properties would fulfill this requirement. Acetylated sub-bituminous coals would contain acetate esters and mixed anhydrides.

Summary

A number of coals of the bituminous and sub-bituminous ranks have been acetylated at 45°C. using acetic anhydride vapor at a relative pressure of unity. Acetylation by this procedure gives hydroxyl contents less than that determined by the trimethylsilyl ether method for bituminous coals but higher hydroxyl contents for sub-bituminous coals. It is suggested that acetic anhydride reacts with carboxyl groups to give mixed acid anhydrides and the higher values obtained for sub-bituminous coal is due to the carboxyl group content of such coals. Oxygen gas catalyzes the acetylation of sub-bituminous coals and until the effect of oxygen is investigated in detail, acetylation of lower rank coals with acetic anhydride should be done in the absence of oxygen.

Acknowledgment

The authors wish to thank BCR, Inc. and the Coal Research Board, Commonwealth of Pennsylvania, for furnishing coal samples and analyses. They also wish to thank Dr. S. Friedman and Dr. Irving Wender, Bruceton Station, U. S. Bureau of Mines, for furnishing coal samples.

References

1. Blom, L., Edelhausen, L., and Van Krevelen, D. W., Fuel (London) 36, 135 (1957).
2. Friedman, S., Steiner, W. A., Raymond, R., and Wender, I., Preprint, Gas and Fuel Division, New York Meeting, September, 1957.
3. Fugassi, P., Masciantonio, P., Trammell, R., Preprint in this volume.